



Supplementary Information for

Oxygen isotope composition of the Phanerozoic Ocean - and a possible solution for the 'dolomite problem'

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Other supplementary materials for this manuscript include the following:

Datasets S1 to S2

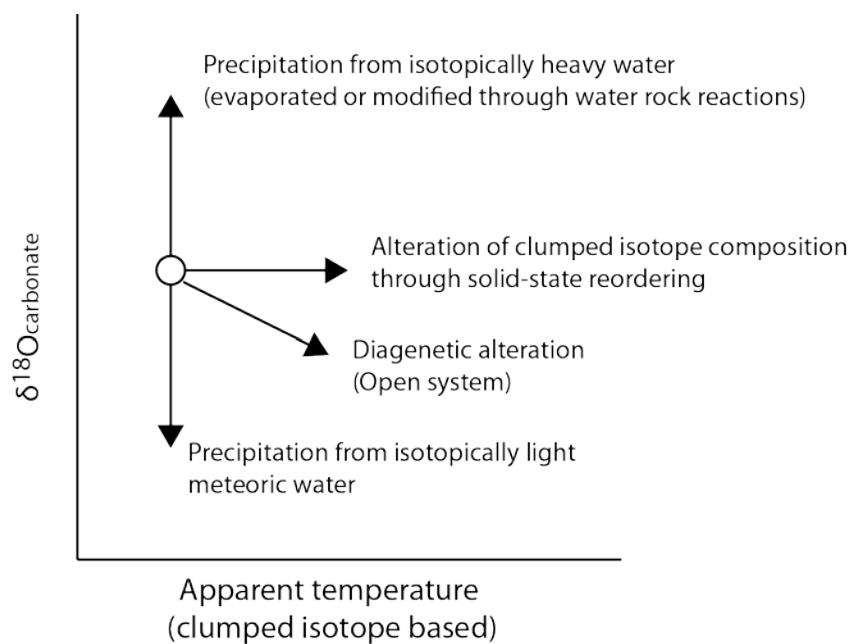


Fig. S1. Figure S1- A schematic diagram demonstrating the effect of different processes over the carbonate bulk isotope composition and the clumped isotope based temperature. Variations in the water composition at or near the Earth surface following evaporation or mixing with meteoric water will affect the $\delta^{18}\text{O}$ of carbonate but not the clumped isotope composition and temperatures calculated from them. Solid-state reordering at elevated burial temperatures alters clumped isotope temperatures towards higher values, without changing the carbonate $\delta^{18}\text{O}$. Diagenetic alteration at elevated temperatures alters both bulk and clumped isotope compositions and can therefore drive the observed anti-correlation between the two variables discussed in the manuscript.

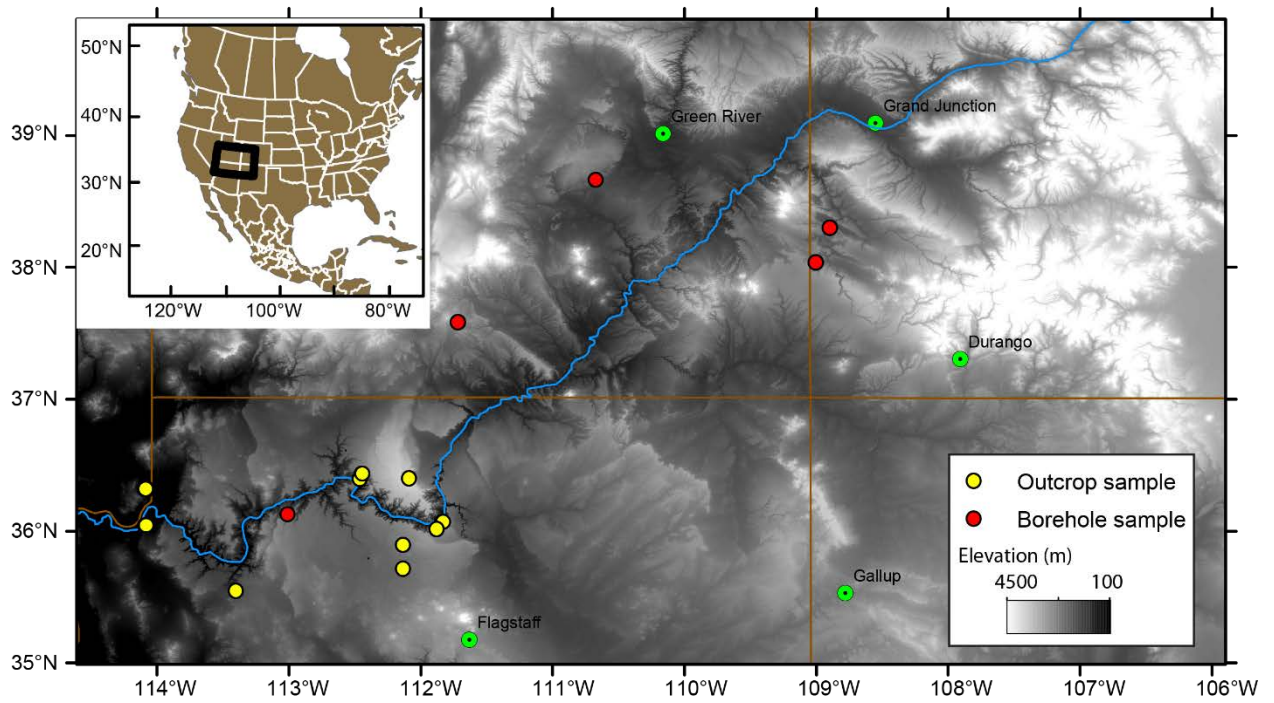


Fig. S2. Digital Elevation model of the Colorado Plateau. The main-stem of the Colorado River is marked by a blue line. Sampling sites are marked yellow for locations where dolomite was collected directly from Paleozoic outcrops, and red for samples collected from boreholes cores.

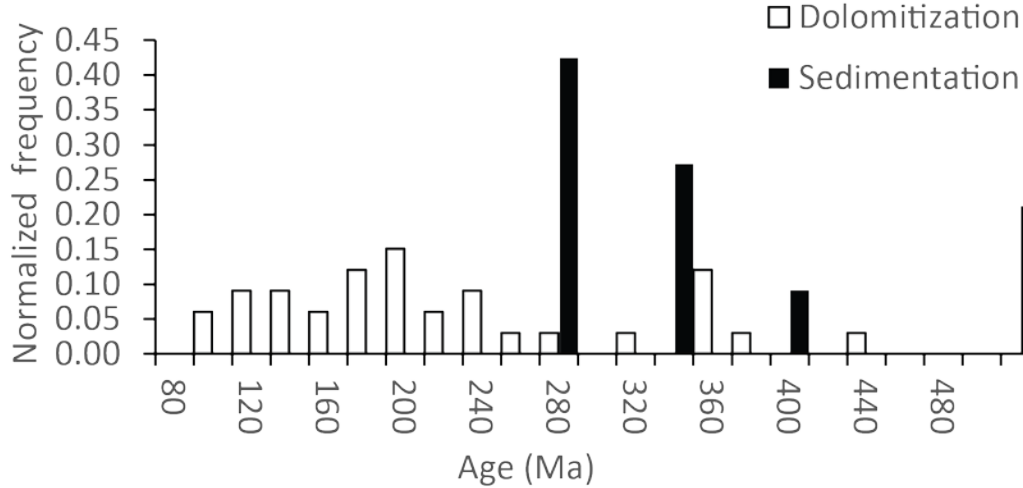


Fig. S3. Histograms of sedimentation and dolomitization ages for dolomite samples from the western Colorado Plateau. Sedimentation ages are the time of deposition of sampled formations (i.e., stratigraphic ages). Dolomitization ages are calculated by assuming a simple thermal history in which deposition at 30°C¹⁻³ was followed by a linear increase of temperature at a rate of 4 °C Myr⁻¹. This thermal history predicts peak burial temperatures at 100 Ma, of 140°C and 80°C for the base of the Cambrian and the top of the Permian surfaces, respectively, and is consistent with thermochronometric constraints on the peak burial conditions at the western Colorado Plateau^{4,5}. The formation temperature of each sample is then used to calculate the time-interval between deposition and dolomitization, and to approximate the absolute time of dolomitization. Importantly, the western Colorado Plateau was uplifted above sea-level at the Late Upper Cretaceous^{6,7}, preventing later Cenozoic dolomitization of the Paleozoic section by interaction with seawater in this region. Calculated dolomitization ages extend from Early Paleozoic to the Late Upper Cretaceous, and demonstrates the wide range of dolomitization ages covered by our data set.

Table S1. Clumped and bulk isotope composition of Paleozoic dolomite samples from the Colorado Plateau, USA. Full data compilation is available in .xls format online (Dataset S2).

sample	Location	Texture/Fabric	Latitude	Longitude	Stratigraphic age (Ma)	Calcite (wt%)	Dolomite (wt%)	n	$\delta^{13}\text{C}$ (‰ VPDB)	+1 S.D.	$\delta^{18}\text{O}$ (‰ VPDB)	+1 S.D.	Δ_{cl} (‰ ARF)	+1 S.E.	T (°C) ⁽¹⁾	+1 S.E.	$\delta^{18}\text{O}_{\text{water}}$ (‰ VPDB) ⁽²⁾	+1 S.E.
CP14	3 Fgnar unit	cement	38.056	-109.003	340	0	100	4	-1.01	0.01	-3.43	0.48	0.485	0.013	125	9	10.7	1.0
CP15a	Se Mohoak Canyon Pipe	cement	36.125	-113.007	270	0	100	2	0.47	0.02	-2.36	0.03	0.545	0.014	86	7	7.3	1.0
CP15b	Se Mohoak Canyon Pipe	cement	36.125	-113.007	270	0	100	4	1.37	0.01	-3.28	0.51	0.605	0.018	57	7	1.9	1.3
CP18	1-2 Utah State	cement	38.661	-110.669	270	0	100	3	1.30	0.01	-1.14	0.53	0.598	0.012	60	5	4.6	0.9
CP2	Wheeler Ridge	cement	36.042	-114.088	505	0	100	3	-0.91	0.00	-4.50	0.56	0.566	0.007	75	1	3.5	0.1
CP21	1 trap canyon	cement	37.583	-111.719	270	0	100	5	3.15	0.00	-6.39	0.41	0.550	0.008	83	4	2.8	0.6
CP23	Paradox injection	cement	38.297	-108.895	340	1	99	4	-1.12	0.01	-2.89	0.05	0.510	0.012	107	8	9.4	0.9
CP24	Paradox injection	cement	38.297	-108.895	340	2	98	4	0.60	0.01	-0.89	0.50	0.579	0.015	69	7	6.3	1.1
CP30a	Azure Ridge	cement	36.318	-114.093	505	1	99	1	-0.92	0.00	-5.42	0.01	0.568	0.016	74	8	2.4	1.2
CP30b	Azure Ridge	vein	36.318	-114.093	505	0	100	1	-0.92	0.01	-6.21	0.01	0.567	0.017	75	8	1.7	1.3
CP35	Azure Ridge	cement	36.316	-114.073	340	0	100	1	2.78	0.00	-1.94	0.01	0.608	0.016	56	7	3.1	1.2
CP37	Azure Ridge	cement	36.317	-114.077	340	0	100	2	1.02	0.06	-12.52	0.12	0.524	0.013	98	8	-1.6	1.0
CP39	Azure Ridge	cement	36.319	-114.085	391	0	100	3	-0.40	0.04	-4.80	0.65	0.551	0.007	83	4	4.3	0.5
CP41(1)	Thunder River Trail	cement	36.434	-112.445	275	2	98	4	2.69	0.11	-10.19	0.60	0.562	0.014	77	7	-2.0	1.0
CP41(2)	Thunder River Trail	cement	36.434	-112.445	275	2	98	3	3.58	0.09	-0.91	0.74	0.610	0.028	55	11	4.0	2.1
CP45c	Thunder River Trail	oids	36.395	-112.458	505	4	96	4	-0.31	0.06	-9.09	0.04	0.561	0.007	78	3	-0.8	0.5
CP46(1)	Thunder River Trail	cement	36.431	-112.440	270	0	100	2	2.28	0.08	0.27	0.34	0.607	0.007	56	3	5.4	0.5
CP46(2)	Thunder River Trail	cement	36.431	-112.440	270	0	100	2	2.83	0.08	2.06	0.21	0.636	0.000	45	0	5.1	0.0
CP4a	Wheeler Ridge	cement	36.042	-114.084	391	0	100	4	-2.64	0.01	-5.55	0.53	0.501	0.005	113	3	7.3	0.4
CP4b	Wheeler Ridge	druse	36.042	-114.084	391	0	100	4	-1.26	0.01	-8.37	0.53	0.515	0.004	104	3	3.3	0.3
CP50a	North Canyon	cement	36.399	-112.085	270	0	100	2	4.63	0.05	1.74	0.09	0.602	0.022	58	9	7.3	1.6
CP57(1)	Tanner Trail	cement	36.066	-111.833	340	1	99	1	1.36	0.00	-5.89	0.01	0.554	0.013	81	7	3.0	1.0
CP58(5)	Tanner Trail	cement	36.067	-111.830	505	2	98	2	-1.00	0.00	-6.02	0.00	0.611	0.029	55	11	-1.4	2.2
CP59	Tanner Trail	cement	36.067	-111.830	505	2	98	2	-0.95	0.01	-6.13	0.02	0.578	0.013	69	6	1.0	1.0
CP61a	Tanner Trail	cement	36.068	-111.829	505	0	100	2	-3.41	0.00	-8.31	0.01	0.543	0.013	87	7	1.3	1.0
CP62	Tanner Trail	cement	36.012	-111.877	270	0	100	2	2.15	0.01	-2.54	0.09	0.614	0.019	53	8	2.0	1.4
CP63	Tanner Trail	cement	36.012	-111.877	270	0	100	2	1.84	0.02	-3.09	0.07	0.592	0.002	63	1	3.1	0.1
CP64a	Plateau	cement	35.890	-112.131	270	0	100	2	4.21	0.00	-0.64	0.08	0.614	0.011	53	4	4.6	0.8
CP64c	Plateau	cement	35.890	-112.131	270	1	99	1	4.75	0.00	1.82	0.01	0.643	0.014	42	5	4.3	1.0
CP65(1)	Plateau	cement	35.890	-112.131	270	0	100	2	4.09	0.20	1.63	0.76	0.617	0.022	41	8	3.8	1.6
CP65(2)	Plateau	cement	35.890	-112.131	270	0	100	2	4.47	0.74	1.73	0.53	0.632	0.011	46	4	5.1	0.8
CP66(1)	Plateau	cement	35.713	-112.131	270	1	99	3	-0.25	0.70	-3.56	0.33	0.618	0.013	52	5	0.6	1.0
CP66(2)	Plateau	cement	35.713	-112.131	270	0	100	3	-0.22	0.10	-2.70	0.14	0.603	0.007	58	3	2.6	0.5
CP66(3)	Plateau	cement	35.713	-112.131	270	0	100	3	-1.53	0.12	-2.48	0.78	0.554	0.017	81	9	6.5	1.3
CP68(1)a	Plateau	cement	35.547	-113.399	340	0	100	3	-1.63	0.12	-4.40	0.18	0.560	0.004	78	2	4.1	0.3
CP68(1)b	Plateau	cement	35.547	-113.399	340	0	100	3	-1.57	0.07	-4.26	0.11	0.535	0.026	92	14	6.1	1.9
CP68(2)	Plateau	cement	35.547	-113.399	340	0	100	3	-3.97	0.13	-5.64	0.19	0.620	0.010	51	4	-1.0	0.7
CP6a	Wheeler Ridge	cement	36.042	-114.084	340	0	100	4	0.42	0.01	-2.95	0.49	0.532	0.006	94	3	6.6	0.4
CP6b	Wheeler Ridge	vein	36.042	-114.084	340	0	100	4	0.46	0.01	-4.66	0.48	0.531	0.011	94	6	6.0	0.8
CP7	Wheeler Ridge	epigenetic	36.041	-114.084	340	0	100	3	0.01	0.01	-12.30	0.56	0.458	0.007	146	6	3.5	0.5

⁽¹⁾ Temperatures calculated using Bonifacie et al.⁸ calibration.

⁽²⁾ $\delta^{18}\text{O}_{\text{water}}$ was calculated using Horita⁹ equation for temperature dependent fractionation between dolomite and water.

References

1. Finnegan, S. et al. The Magnitude and Duration of Late Ordovician-Early Silurian Glaciation. *Science* 331, 903-906, doi:10.1126/science.1200803 (2011).
2. Cummins, R. C., Finnegan, S., Fike, D. A., Eiler, J. M. & Fischer, W. W. Carbonate clumped isotope constraints on Silurian ocean temperature and seawater $\delta O-18$. *Geochim Cosmochim Acta* 140, 241-258, doi:10.1016/j.gca.2014.05.024 (2014).
3. Came, R. E. et al. Coupling of surface temperatures and atmospheric CO₂ concentrations during the Palaeozoic era. *Nature* 449, 198-U193, doi:10.1038/nature06085 (2007).
4. Dumitru, T. A., Duddy, I. R. & Green, P. F. Mesozoic-Cenozoic Burial, Uplift, and Erosion History of the West-Central Colorado Plateau. *Geology* 22, 499-502, doi:10.1130/0091-7613(1994)022<0499:Mcbuae>2.3.Co;2 (1994).
5. Flowers, R. M., Wernicke, B. P. & Farley, K. A. Unroofing, incision, and uplift history of the southwestern Colorado Plateau from apatite (U-Th)/He thermochronometry. *Geol Soc Am Bull* 120, 571-587, doi:10.1130/B26231.1 (2008).
6. Flowers, R. M. & Farley, K. A. Apatite He-4/He-3 and (U-Th)/He Evidence for an Ancient Grand Canyon. *Science* 338, 1616-1619, doi:10.1126/science.1229390 (2012).
7. Wernicke, B. The California River and its role in carving Grand Canyon. *Geol Soc Am Bull* 123, 1288-1316, doi:10.1130/B30274.1 (2011).
8. Bonifacie, M. et al. Calibration of the dolomite clumped isotope thermometer from 25 to 350°C, and implications for a universal calibration for all (Ca, Mg, Fe)CO₃ carbonates. *Geochim Cosmochim Acta*, doi:http://dx.doi.org/10.1016/j.gca.2016.11.028 (2017).
9. Horita, J. Oxygen and carbon isotope fractionation in the system dolomite-water-CO₂ to elevated temperatures. *Geochim Cosmochim Acta* 129, 111-124, doi:10.1016/j.gca.2013.12.027 (2014).